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SOL-GEL PROCESSED MULTIFUNCTIONAL ORGANIC POLYMER-  
INORGANIC OXIDE COMPOSITES FOR ELECTRONICS AND  
PHOTONICS

FINAL REPORT

January 1992

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POLYMER-INORGANIC OXIDE COMPOSITES FOR ELECTRONICS  
AND PHOTONICS

**PRINCIPAL INVESTIGATOR:** Ryszard Burzynski, Ph.D.

**INCLUSIVE DATES:** 06-01-91 to 01-31-92

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### ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This document includes a detailed description of efforts to develop sol-gel/polymer composites for use in the fields of electronics and photonics. The central aim of the SBIR Phase I effort was to develop a multifunctional composite containing both oxides and organic polymers; both of the components in these materials are expected to perform active roles.

A particular example that was investigated is one in which the inorganic component increases the charge carrier mobility while an organic component enhances its nonlinear optical response. Another example is the potential of organic and inorganic semiconductors becoming redox-coupled creating an entirely new class of multifunctional materials. The work involved (1) the synthesis of several vanadium alkoxides and polymers, (2) developing protocols for the preparation of composite films of the highest optical quality, and (3) obtaining assessments of conductivity and nonlinear optical response.

Spectroscopic data indicate the presence of specific absorption bands characteristic of charge transfer phenomena. High conductivity and a nonlinear optical response of the composites were observed. Further development and optimization of these systems will yield materials useful in such applications such as photorefractive media, antistatic coatings, large area electroluminescent panels or light emitting devices.

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## 1. EXECUTIVE SUMMARY

The accomplishments of the last twenty years and the tremendous potential of optical data processing have all but assured the future use of photonic materials. The development of materials to perform high frequency operations will determine how soon there is a full scale implementation of these systems. The growth of this field is clearly dependent upon the ability of researchers to prepare advanced materials. Sol-gel/polymer composite materials are a novel way of blending the superior conventional optical properties of inorganic glasses with the synthetic flexibility and dynamic optical properties of organic polymers.

The results of a six month SBIR Phase I research contract involving sol-gel composite materials is presented in this document. The general goal of this research program was to test the feasibility of producing novel multifunctional composite materials for photonics and electronics and to identify the most promising applications which will be pursued in the Phase II development. The proposed research involves a unique processing technique yielding final materials in which both the organic and inorganic components perform active roles. An example of such a system that was investigated is one in which the inorganic component increases the *charge carrier mobility* while an organic component enhances its *nonlinear optical response*. Another example is the potential of organic and inorganic semiconductors becoming redox-coupled creating an entirely new class of materials. Sol-gel processing has been chosen for this research approach because of its proven reputation for producing homogeneous materials (liquid mixing), the relatively low temperatures which are required to produce these composite glasses, and the ability to produce novel interactive composites containing glasses, polymers and dopants.

During the time provided in a Phase I research effort, several systems have been identified as having specific chemical interactions. The out-of-plane conductivity of PTV/ $V_2O_5$  films was measured to increase by eight orders of magnitude over a comparable pure PTV sample. The presence of such high conductivity and, hence, very high charge carrier mobility in a composite containing polymers (having proven to be effective nonlinear optical materials) is very promising. Further development and optimization of these systems will yield materials that have the potential to perform in technological applications such as *photorefractive media*, *antistatic coatings*, *large area electroluminescent panels* or *organic based light emitting devices*.

### 1.1. Summary of Phase I Research

Laser Photonics Technology's staff has successfully developed a novel method of combining organic compounds with inorganic oxide gels which has led to a new class of materials. This process has tremendous potential in creating multifunctional materials for applications in photonics, electronics, medicine, engineering, etc. The uniqueness of this approach provides that: (1) one may select the most appropriate functional group or atomic component for a particular task and incorporate it into a composite, (2) the components can be homogeneously combined in a liquid phase, (3) organic polymers and sol-gel components can be mixed in

virtually any ratio, (4) the entire process can be performed at relatively low temperatures, and (5) the addition of polymers to the sol-gel glasses enables films to be made considerably thicker ( $>0.4$  microns) which not easily can be prepared from pure oxides due to unavoidable cracking.

In the completion of this contract a number of systems were prepared that varied in molecular composition. This work involved the synthesis of some organic and inorganic components and the subsequent fabrication of thin composite films for conductivity and nonlinear optical measurements. The staff of LPT, Inc. has successfully demonstrated the:

- 1) Synthesis of vanadium alkoxides including: vanadium butoxide oxide, vanadium triisopropoxide oxide, and vanadium tri(t-amylxy) oxide
- 2) Synthesis of poly(thienylene vinylene) -(hereafter abbreviated PTV)- capable of being processed with sol-gel metal alkoxides
- 3) Preparation of pure polyacrylonitrile (hereafter abbreviated PAN) films, pure vanadium oxide films, PAN/vanadium oxide films
- 4) Composite films containing PTV and poly(2,5-dimethoxyphenylene vinylene) - (hereafter abbreviated DMPPV)- polymers and vanadium pentoxide
- 5) Spectroscopic characterization of the above films was performed in order to determine what optical frequencies might be used in device applications and to potentially identify specific interactions between selected components
- 6) Conductivity measurements were made in order to assess the conductive nature of the organic/inorganic semiconductor composites
- 7) Assessments of the third order nonlinear optical susceptibility of selected samples

The specific aims of this research project were to explore the feasibility of preparing novel sol-gel composite materials in which both, the inorganic and organic component would actively enhance the material's properties useful in photorefractive materials, antistatic coatings or light emitting devices. As an example, vanadium pentoxide gels were sol-gel synthesized and combined in the liquid phase with various conjugated polymer structures to establish the possible formation of inorganic-organic semiconductor structure through a redox coupling mechanism. All of the materials required for testing were prepared and evaluated in addition to several configurations not directly mentioned in the original proposal. The body of this document contains detailed information on the preparation of these materials and the specific conditions where optimum performance could be obtained. These systems contain numerous components, react at variable rates, and require a high degree of quality control since even subtle variations in procedure or composition can easily affect the optical clarity and overall quality of the final product.

One particular system chosen to demonstrate the general objectives is the fabrication of multicomponent sol-gel composite materials through coupling vanadium pentoxide and selected conjugated polymers. It is of particular interest to introduce organic polymers with large nonlinear optical response in a solution of vanadium oxide gel with the goal of initiating a specific chemical interaction and assess the degree to which these values are retained or



improved by virtue of their presence in this composite structure. In addition, data are presented indicating a many-fold increase of the composite conductivity over that of the pure polymers. Additionally, it was important to assess the ability of these materials to form thin films and be of good optical quality in order to be applicable in photonics or electronic devices such as photorefractive media or light emitting devices.

Extensive experimental research performed by LPT produced substantial groundwork for subsequent development of multifunctional photonics/electronics materials based on sol-gel composites. The feasibility of synthesizing novel semiconductor inorganic oxide/organic polymer composites by sol-gel processing technique has been established. The goal of developing a interactive inorganic/organic composite is a genuinely innovative method of which little is known; it is clear that many parameters in sol-gel processing of these materials need to be further optimized. The report discusses accomplishments in these areas and offers *recommendations on how to resolve these challenges*. The achievements and recommendations will form the basis for subsequent Phase II effort leading to commercialization of these materials.

## 2. SOL-GEL COMPOSITES

### 2.1 Molecular Components

The sol-gel composites that are the subject of this report are extremely versatile in their composition, processing and, consequently, their physical and mechanical properties.

The uniqueness of this approach provides that one may select the most appropriate functional group or atomic component for a particular task and incorporate it into a composite of chosen physical and/or mechanical properties. The components are combined in a liquid phase ensuring that the final product will be homogeneous. Organic polymers and sol-gel components can be mixed in virtually any ratio necessary to obtain the desired properties. The entire process can be conducted at relatively low temperatures enabling the incorporation of even the most sensitive compounds. The addition of polymers to sol-gel glasses enables films to be made considerably thicker and of excellent optical properties.

### 2.2 Principal Methods

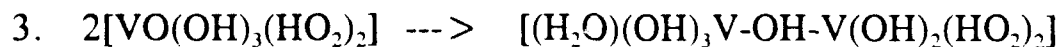
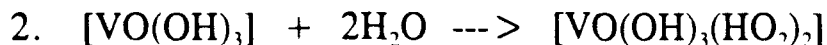
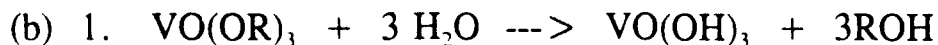
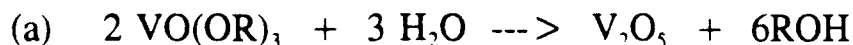
Preliminary work involved extensive studies of numerous sol-gel precursor/organic compositions in order to evaluate the compatibility of the different components in various solvents.

The first step in our procedure to develop sol-gel composites is the full or partial hydrolysis of the principal alkoxide which in all cases was either VIPO (vanadium triisopropoxide oxide) or VTAO (vanadium t-amylalcohol oxide). Even with this first, and somewhat trivial reaction, important choices must be made with respect to reaction conditions. The rate of hydrolysis has been clearly shown to be a function of the pH<sup>1</sup>. In addition, this has a decidedly important effect upon the eventual microstructure of the matrix<sup>2</sup>. Since there are fundamental immiscibilities between alkoxides and water, it is a common practice to add ethanol or isopropanol during this step. While these additions function to solve this problem, their presence often has deleterious effects upon the final product. It is our experience that a minimum amount of externally added alcohols or co-solvents should be added since they must eventually be removed. This is particularly true in spincoating and fiber forming procedures.

Another important consideration is the H<sub>2</sub>O/alkoxide molar ratio (subsequently referred to as, r). The hydrolysis and polycondensation reactions proceed conceptually more simply if this ratio is 3 as seen in Figure 1. It can be seen that if the ratio is 1.5, these reactions are ultimately completed, though the final hydrolysis reactions depend upon the products of the initial polycondensation reactions. Reducing the water/alkoxide ratio has three principal functions: (1) water becomes the limiting reagent in the reactions which effectively slows down the initial hydrolysis and affects the rate of condensation, (2) there is less water left behind in the matrix which may reduce the tendency for immiscible components to segregate and (3) there is less

shrinkage associated with drying.

Vanadium alkoxides can be hydrolyzed very easily; this arises from the high electrophilic power of the vanadium atom and the possible coordination expansion from 4 to 5 or 6. Hydrolysis rates can generally be decreased by introducing alkyl groups capable of providing steric hindrance. This can be seen to be true of all sol-gel precursors independent of the alkoxide metal. Given these facts and considerations, two particular parameters can be seen to control the formation of  $V_2O_5$ : the molar ratio of water to alkoxide,  $r$ , and the number and nature of the alkoxy groups. In order to obtain the stoichiometric hydrolysis of vanadium alkoxide,  $r$ , should be equal to 3 (see Figure 1). However, alkoxy groups, particularly those of low molecular weight, are released upon hydrolysis and can react with freshly formed vanadium pentoxide resulting in the formation of  $V^{+4}$  species. These species are always present in freshly synthesized  $V_2O_5$  and play an important role in the formation of  $V_2O_5$  gels since it is known that they act as polymerization initiators<sup>3</sup>. General hydrolysis and condensation processes (eqn.(a) in Figure 1) can be more precisely described as, first, the formation of neutral precursors such as  $VO(OH)_3$  (eqn. (b1) in Figure 1), followed by the coordination expansion of the vanadium atom through the incorporation of additional water (eqn. b2) and, finally, condensation (removal of water) and the formation of the V-O-V bond. This sequence of events leads to the formation of chain polymers and, finally, to ribbon like fibers which have been previously characterized<sup>4</sup>.



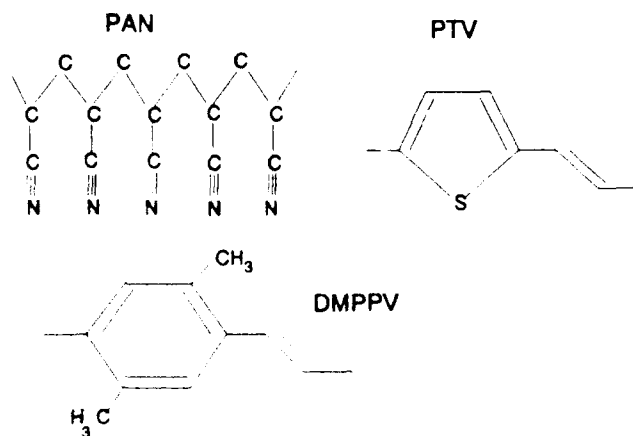
**Figure 1.** Fundamental hydrolysis and polycondensation reactions in sol-gel processing of vanadium alkoxides.

The main feature of this novel sol-gel/polymer processing technique is that it permits the formation of composites containing not only  $V_2O_5$ , but also  $SiO_2$ ,  $TiO_2$  (or virtually any inorganic oxide) and one of several organic polymers. Furthermore, other dopants (both organic and inorganic) can be added to tailor the linear and nonlinear optical properties of the material. Once all the oxides have been added with enough water to fully hydrolyze all the components one has between a few hours and several weeks before the viscosity has risen to levels that make the film preparation too difficult to work with. This time will be dependent upon the amount of solvents that are used, the amounts and types of alkoxides and environmental parameters such

as temperature and humidity. Minor adjustments to the macroscopic viscosity can be made with additions of solvent though one must keep in mind (1) the deleterious effects of excess solvent and (2) the polymeric nature of the sol-gel sample and that the preparation is not infinitely dilutable.

The incorporation of an organic polymer should occur as soon as possible to ensure the greatest likelihood of obtaining a homogeneous final product. It is very important that the solvents are chosen such that the polymer is sufficiently soluble and that its incorporation does not cause an undesirable effect upon the optical clarity of the resulting solution. These consequences are presumably a function of either (1) the insolubility of certain intermediates or final products in the solvent(s) or (2) the growth of oxide aggregates or "beads" at or about the wavelength of visible light. The volatility and surface tension of the solvents can have a significant influence upon the spreading behavior of the solutions used in spincoating.

The LPT staff has successfully prepared several sol-gel/polymer composites over the duration of the project. Except for discovering appropriate solvents, each of the polymers was readily incorporated into the composite. There are certain limits to the amount of polymer that one must add to achieve crack-free films in excess of  $0.4\mu\text{m}$  in thickness. As has been previously mentioned, polymers serve to mitigate the processes which lead to visible cracks. The majority of the preparations contained less than 50% polymer by weight since it was our intention to illustrate the virtues of the composite. Among the polymers that were incorporated are PTV, PAN, DMPPV.



**Figure 2** Structures of polymers used in sol-gel processing.

### 3. INORGANIC-ORGANIC COMPOSITE SYSTEMS.

Hydrolysis and condensation of vanadium oxo-alkoxides results in the formation of vanadium pentoxide gels. The synthesis of an alkoxide can be accomplished by refluxing a mixture of ammonium vanadate and alcohol. The higher conjugated alcohols proved to give higher yields of alkoxides due to their superior chemical stability (especially inadvertent hydrolysis and decomposition). Our efforts, therefore, were concentrated on t-amyl alkoxide (*vanadium tri(tert-amyloxide) oxide*) resulting in vanadium triisopropoxide oxide.

Polyacrylonitrile (PAN) and poly(thienylene vinylene) (PTV) polymers were successfully incorporated into vanadium pentoxide gel yielding good optical quality films when dried at temperatures less than 100°C in an inert (argon and nitrogen were found to be equally effective) environment. These films were then thermally annealed at about 300°C in an inert environment for periods of up to four hours to insure complete conversion of vanadium gel to V<sub>2</sub>O<sub>5</sub>. The dark films were then assessed for their electrical and optical properties.

#### 3.1 Synthesis of Vanadium Alkoxides.

a. General reaction scheme:

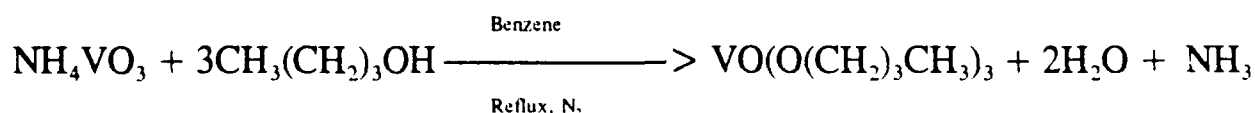


The procedure used<sup>5</sup> is an improved method originally described by Prandl and Hess<sup>6</sup>. Three moles plus excess of high grade alcohol was refluxed with one mole of ammonium vanadate (NH<sub>4</sub>VO<sub>3</sub>) under a 90 cm long, glass packed column. When a majority of the excess alcohol was removed by azeotropic distillation, the reaction was cooled down and stopped. The remaining unreacted solids and decomposition products were collected by a centrifuge and the remaining alcohol was vacuum distilled off.

b. Specific reaction schemes.

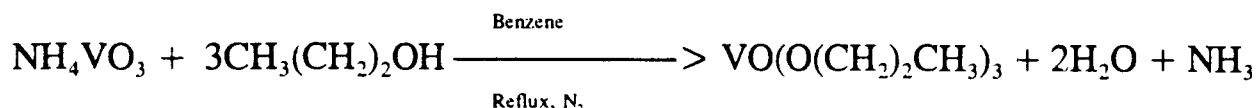
##### 1. 1-Butanol

The first alcohol attempted was 1-butanol. High grade 1-butanol was purchased and kept closed until the reaction was initiated. The reaction was carried out according the following procedure:



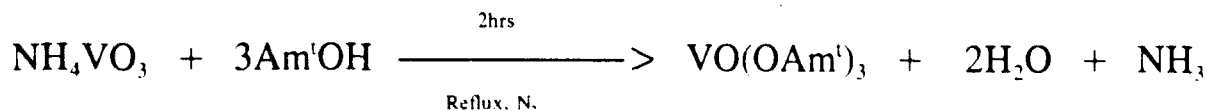
11.7 g (0.1 mole) of  $\text{NH}_4\text{VO}_3$  is dissolved in benzene (50 ml) in an argon flushed, oven dried, 3-neck 100 ml flask equipped with a magnetic stir bar. 25 g (0.3 mole) of 1-butanol is added and the flask is immediately fitted with a dry nitrogen inlet and a 20 cm reflux condensor. The reaction is refluxed for 2 hours at which time there was no obvious signs of a reaction. The reaction was then allowed to proceed for 24 hours under an inert atmosphere after which time the reaction vessel still contained a large amount of solids. The reaction mixture was then distilled. The first fraction, received at  $78^\circ\text{C}$  to  $85^\circ\text{C}$  was an alcohol-water azeotrope. The second fraction distilled at  $115^\circ\text{C}$  to  $120^\circ\text{C}$  was cloudy and white in appearance and smelled of ammonia. The third and last fraction came off at  $100^\circ\text{C}$  under vacuum and produced a white precipitate upon cooling. An infrared spectrum taken of each fraction failed to show the characteristic  $\text{V}=\text{O}$  vibration band at  $1020\text{ cm}^{-1}$ . Each fraction was treated with water in order to determine if hydrolysis could be initiated. It was concluded after several attempts that using 1-butanol as a reagent demanded very strict control over the reaction conditions - details which were not published. These conditions included the length of the reflux column, reaction duration, and choice of the starting solvent. Several new parameters were attempted, but only a small quantity of vanadium butoxide oxide was obtained. It was concluded that this reaction was difficult to complete with high quality yields, and that the use of a more reactive alcohol would permit significantly higher yields.

## 2. 2-propanol



Since 1-butanol proved to give low yields of alkoxides, it seemed obvious to choose a new alkyl group in order to reduce the steric hinderance in the reaction; this theory proved to be correct. However, the vanadium alkoxide (isopropoxide) needed even more rigorous reaction control due to its extreme reactivity. The unoptimized reaction generated a large amount of decomposition and hydrolysed products. The extreme reactivity of vanadium triisopropoxide oxide made it very difficult to use since it was observed to interact with UV light, heat, air and moisture. Therefore, in order to identify a synthetic route with more favorable reactivities, 2-propanol was abandoned for a more conjugated alcohol.

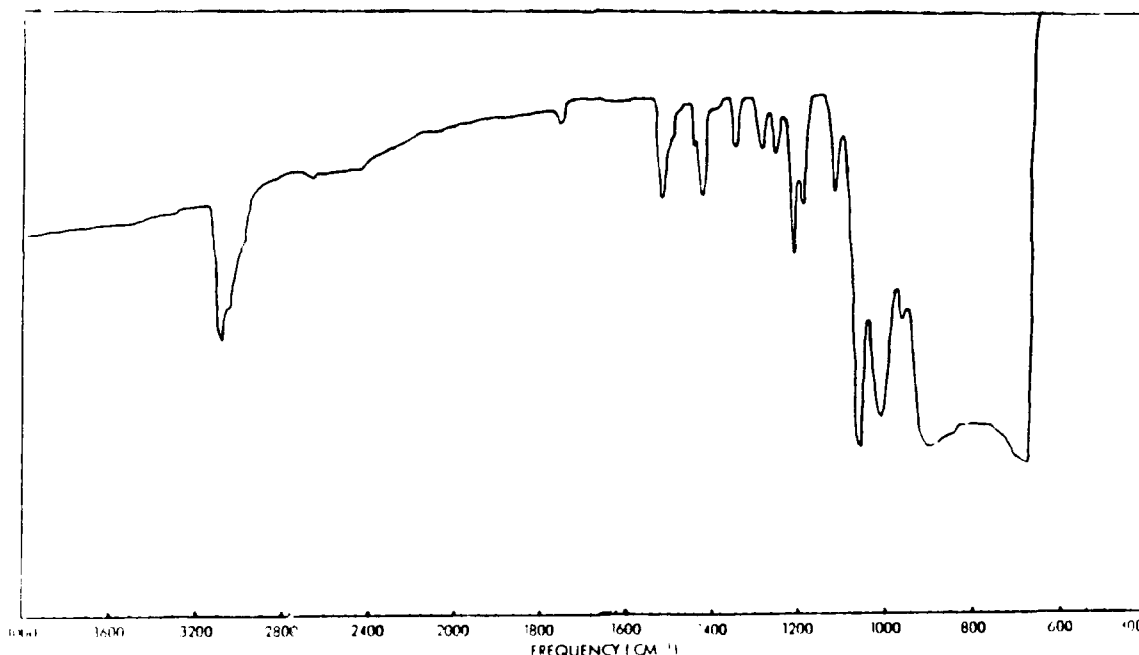
## 3. t-amyl alcohol

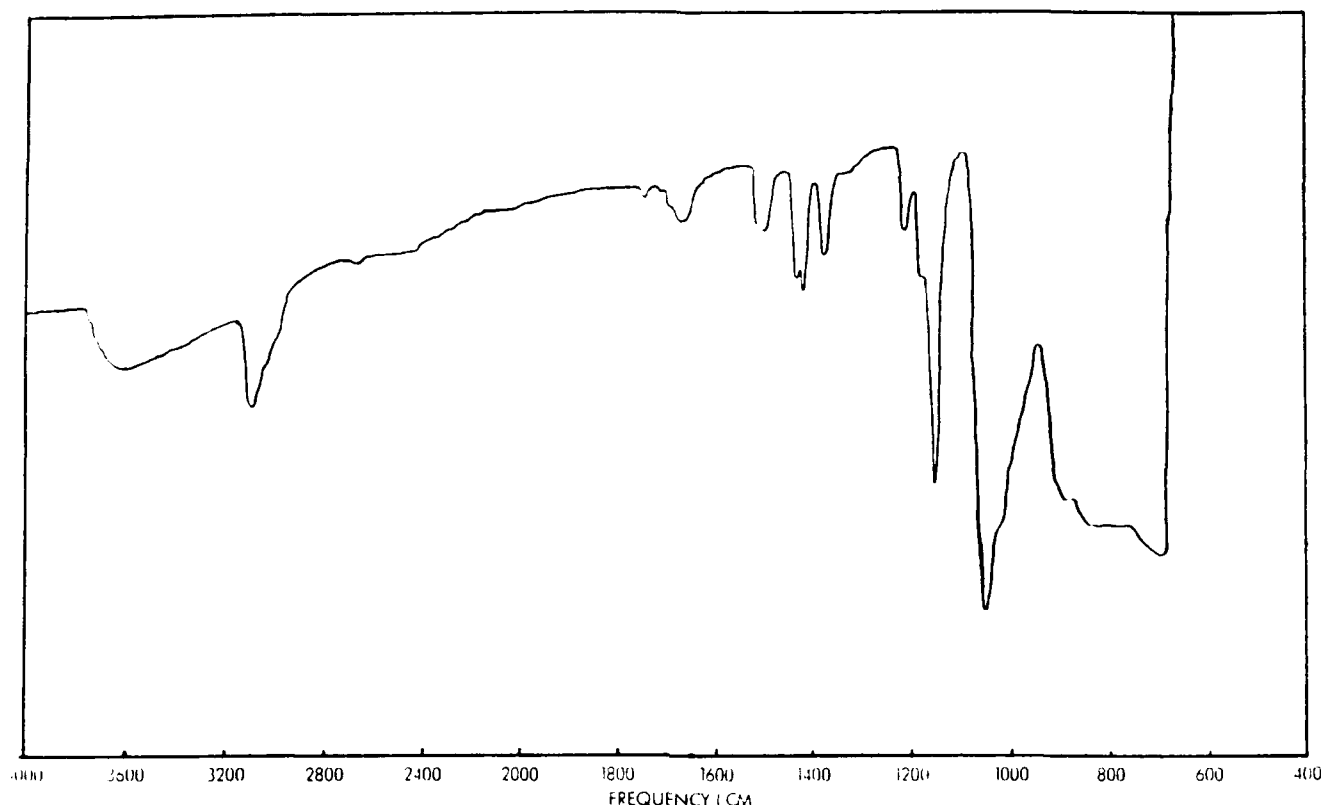


t-Amyl alcohol was the best of the reactants attempted. A large excess of alcohol was used in the absence of any other solvent. The reaction flask required careful preparation. A 3-neck 100 ml flask was dried in oven under an argon flush. The reaction involved refluxing 0.57 moles (50 g) high purity grade t-amyl alcohol under argon with 0.085 moles (10 g)  $\text{NH}_4\text{VO}_3$ . The reaction vessel was equipped with A 90 cm glass packed column. As the reaction progressed the alcohol/water azeotrope is distilled off for approximately 2 hours (some alcohol still remained) and then the reaction temperature is lowered. The remaining solids are removed by filtration. The rest of the unreacted alcohol is removed from the filtrate at room temperature under vacuum resulting in a 55% yield (3.3 ml) of the alkoxide. The final product of this reaction is very hygroscopic (susceptable to hydrolysis and condensation); however, it can be safely stored at  $0^\circ\text{C}$  in the dark.

A few important procedures are required to properly complete the reaction and deserve to be specifically mentioned.. First, the reaction can not be distilled to dryness without the final product instantaneously decomposing. Some amount of remaining excess alcohol must be left before the room temperature vacuum distillation procedure. Second, the length of the packed column was observed to affect the reaction rate. The reaction proceeded without difficulty when the length of the glass packed column was greater than 20 cm. Although water is a by-product of the reaction, the reaction must be protected from air with the use of nitrogen purge. The final product is extremely reactive towards hydrolysis and therefore requires appropriate packaging and handling.

UV-VIS and infra-red spectra of the synthesized alkoxide were acquired to identify the compound. Figure 3 (a) depicts the IR spectrum of vanadium tri(amyloxy) oxide; the spectrum (b) is of commercially available vanadium tri(isoprpxide) oxide and is shown for comparison.





**Figure 3.** (a) IR spectrum of synthesized vanadium tri(*terramyloxyde*) oxide.  
(b) IR spectrum of vanadium tri(isopropoxide) oxide.

### 3.2 Synthesis of PTV Precursor

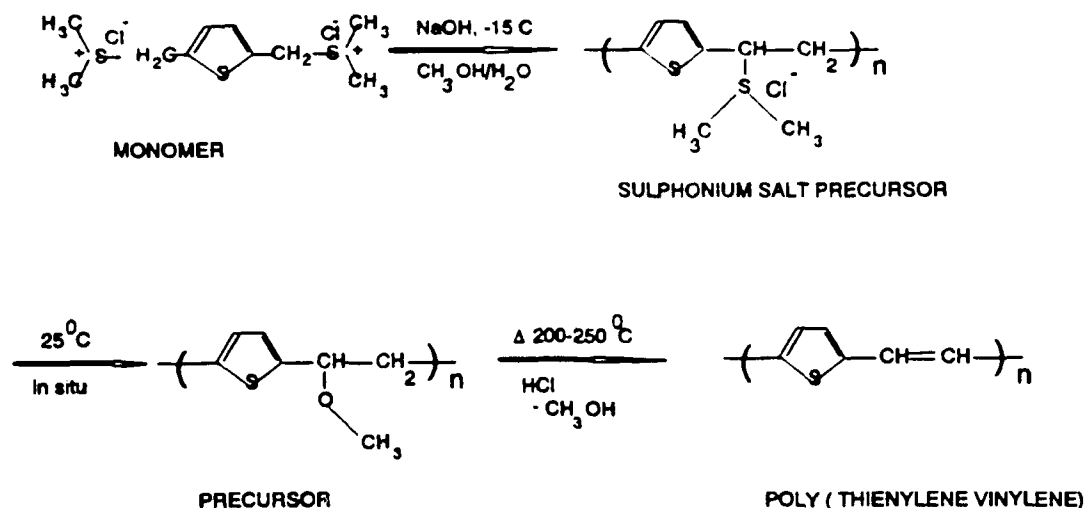
The PTV precursor was obtained by the polymerization of the sulphonium monomer, 2,5-thienylene bis(methylene-dimethyl sulphonium chloride). The quality of the resulting PTV polymer films, and the solubility and stability of the precursor in organic solvents greatly depended on reaction conditions.

#### a. synthesis

The synthesis of PTV polymer was carried out as follows:

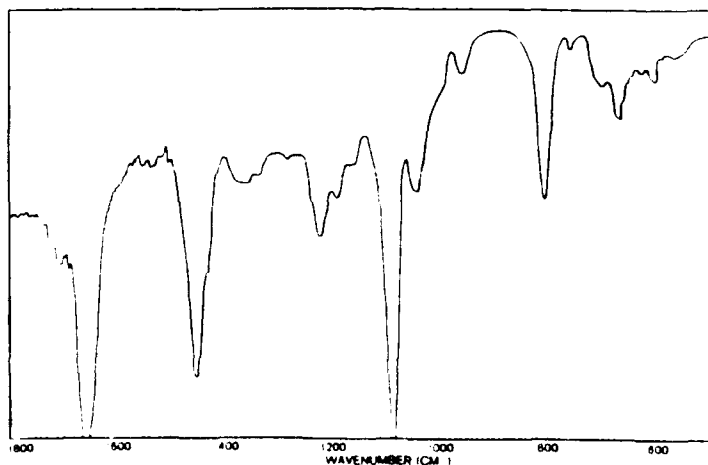
PTV monomer (1.787 g, purchased from Lark Enterprises) was dissolved in 10 ml of 50% (vol) water/methanol mixture. This solution was filtered for undissolved monomer impurities (as the monomer aged, the impurities were observed to increase) and subsequently purged with nitrogen for two hours in the reaction vessel to remove oxygen. The reaction flask was kept at -15 °C utilizing a water/acetone-salt bath. A chilled and nitrogen purged solution of NaOH in water (12.5 ml, 0.4 mol) was added dropwise over 10 min, turning the solution to a light yellow color increasing in hue depending upon the reaction's progress. After 4 hrs at -15



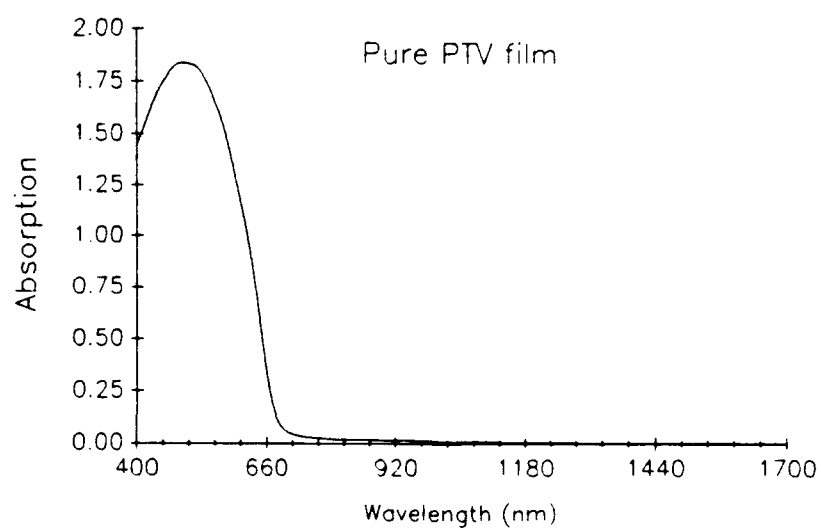


**Figure 4** Synthesis of poly (thienylene vinylene) through soluble precursor.

$0^\circ\text{C}$  the reaction was neutralized with HCl (8.3 g) and allowed to warm to room temperature. The sulphonium salt precursor was allowed to react with methanol at room temperature for 2 hrs. The resulting gelatinous precipitate was collected and immediately placed in one of several polar organic solvents. The solubility increased in the order: THF <  $\text{CH}_2\text{Cl}_2$  < DMF. However, a large percentage of the precipitate remained insoluble and was ultimately discarded. The final product was purified by precipitating it out with the addition of diethyl ether or methanol with a yield of about 10% for the entire reaction. The infrared spectrum of the precursor is consistent with those published in the literature<sup>7</sup> (see Figure 5); the UV spectra of PTV films show characteristic broad band absorption with an energy gap at 1.75 eV (see Figure 6).



**Figure 5.** Infra-red spectrum of PTV sulphonim salt precursor.



**Figure 6** UV-VIS spectrum of fully converted PTV film

### 3.3 Preparation of Composite Films

#### a. Pure PAN

Polyacrylonitrile is a polymer insoluble in all the solvents/solutions attempted except for DMF. The incorporation of PAN into sol/gel preparations was difficult because of the inability to use conventional solvents and cosolvents. Very thin films of  $\text{SiO}_2$ - $\text{TiO}_2$ /polymer can be made, however thicker ones had a tendency to exhibit cloudiness. This optical distortion is attributed to the two factors: (i) the presence of minute amounts of water and (ii) the fundamental incompatibility of the produced blend.

Vanadium alkoxides have an extremely high hydrolysis rate, swelling with water and, to a large extent, retaining it. The incorporation of PAN into vanadium oxide gel films was found to be much easier to accomplish.

The key to making a thick pure PAN polymer films is to minimize exposure of the undried film to moisture. The solvent, DMF must be clean and dry (molecular sieves). Solutions of PAN in DMF (2.5% to 10% by weight) were used in our preparations.

Spin coated or poured films on a clean glass slides were placed in a preheated oven at about 250 °C, which was previously purged with a dry gas (nitrogen or argon). Once dry, the film begins its conversion to a ladder polymer if it is not removed from the oven immediately. The film must then be stored in a desiccator to ensure complete dryness. Once dry, the film is safe from the inadvertent exposure to the moisture in air. This procedure can also be repeated on a very hot hotplate, while flooding the film surface with nitrogen or argon gas.

#### b. Pure Vanadium Sol-Gel Films

Exposure of hydrolysed vanadium alkoxides to heat results in spontaneous reduction of vanadium pentoxide and the films color changing to green. The change of color is caused by formation of  $\text{V}^{+4}$  species in small concentrations (approximately 1 %<sup>8</sup>), though this concentration can be upwards to 10% when the synthesis is performed in an organic solvent <sup>9</sup>.

If reducing the gel forming vanadium pentoxide isn't desired, organic solvents should be minimized and the processing ovens flushed with inert, moisture free gases during the drying process. Interestingly, incorporation of PAN polymer into hydrolyzed vanadium alkoxides was found as the best protective measure against vanadium reduction.

Vanadium alkoxides were hydrolyzed in an ethanol/water solution using a 3:1 and 100:1 water to vanadium molar ratios. The infrared spectra showed that there were no significant differences between these two approaches, except for the presence of different amounts of water. UV-VIS spectra revealed a higher absorption in the 3:1 hydrolysed films over the 100:1 ones

due largely to the higher concentration of vanadium pentoxide. Orange gels were formed from 100:1 hydrolysed vanadium alkoxides, while a deeper red gel formed from 3:1 mixtures. It has been shown that when the molar ratio is less than 1:1, molecular oligomers of vanadium oxide are formed being about 10 Å in diameter and that the orange gels should be considered to be polymeric alkoxo-oxides of the formula  $[V_2O_5 \cdot x(OR^n)_x]_n$ <sup>10</sup>.

When vanadium alkoxides are placed in alcohols, yellow precipitates form, which are assumed to be a mixture of complexes of the type:  $VO(OR)_3(OR')_x$ , where R' is derived from R'OH. The addition of water ( $r > 3$ ) eventually hydrolyses these complexes and the solution is transformed into a red gel after about 30 minutes of vigorous stirring.

The preparation of vanadium pentoxide gels and organic polymer blends requires additional skills since the polymers are not readily dissolved in water. There is, however, a need to use sufficient water to obtain the full hydrolysis of vanadium alkoxide and form  $V_2O_5 \cdot 1.8H_2O$  without precipitating the insoluble polymer. Since vanadium complexes swell and hold large volumes of water, this seems to be helpful in our preparative attempts.

*Procedure for making 3:1 hydrolysed pure vanadium films.*

Methanol (2 g) is mixed with 44 mg of water. Vanadium isopropoxide oxide (10 mg) is added to this solution. A yellow precipitate quickly forms, but turns into a red clear solution after 30 minutes of stirring at room temperature. The addition of 500 mg of cyclopentanone serves to improve the spreading characteristics of this solution. Films are cast on ordinary glass microscope slides and are allowed to dry at 25 to 50 °C culminating in the production of clear red films with a yellowish tint. The thickness of such films is no greater than one micron. The films will turn greenish when heated or if exposed to ambient conditions; this greenish color will become obvious in a matter of a few days.

*Procedure for making 100:1 hydrolysed pure vanadium films.*

Thick films are very difficult to produce when the molar ratio of water to vanadium exceeds 100. High water dilutions result in low concentrations of vanadium complexes. The best procedure thus far is to mix 1 g of methanol with 80 mg of vanadium isopropoxide oxide to form a yellow precipitate. Water (2 grams) is added which instantly results in a reddish colloidal solution. This solution is vigorously shaken and then placed in an ultrasonic bath. Upon ultracentrifugation, a deep red and viscous gel forms. About 1 g of this gel is diluted with 1 g of water and mixed until the colloidal precipitates dissolve; the resulting solution is then filtered through a 1 micrometer filter. The solution is then used to cast the films on glass substrates by either spin coating or spreading. Even though the alkoxide is fully hydrolysed, the film forming vanadium complex will eventually undergo some degree of reduction (turning green) upon exposure to light or heat over long period of time (several hours).

### c. PAN/Vanadium Oxide Films

The easiest method of producing a PAN/vanadium blend is to simply add the vanadium alkoxide directly to a 5% (wt) solution of PAN in DMF. This solution immediately turns red (indicating fast hydrolysis of the vanadium alkoxide) and begins to gel. A film must be poured or spun as soon as the solution is homogeneously mixed. Orange films can be made very thick and clear. The concentration of vanadium can be varied to virtually any degree. The application of heat over 250 °C for 2 hrs will turn the film to a dark brown color. Thinner films with a high concentration of vanadium will turn greenish indicating the presence of the  $V^{+4}$  species. Argon flushing during the drying step minimizes the formation of the green color.

A red gel indicates the hydrolysis of the vanadium alkoxide. However, this may happen even in the absence of water. At first, it was thought that the solvent contained enough water to explain the hydrolysis of the alkoxide. However, when vanadium isopropoxide oxide was placed in DMF, the solution only turned slightly yellow. The addition of water to DMF only turned the solution to orange. Therefore, there is sufficient evidence for a specific interaction between the vanadium alkoxide and the polymer.

Hydrolysis of the vanadium complex was performed in a water/alcohol solution and by a PAN/DMF solution in order to study the difference between these two preparations. UV-VIS spectra revealed only minute differences in absorbance while IR spectroscopy showed no difference at all. Both solutions appeared similar except for the greater viscosity of the PAN /vanadium blend.

Using water in the preparation of polymer/vanadium gel blends was a very difficult task (especially in conditions where  $r > 100$ ) due to the insolubility of the PAN polymer. Without the desired gel viscosity provided by PAN, thick films of hydrolyzed vanadium were very difficult to prepare. The addition of vanadium alkoxide to cyclopentanone caused an immediate reaction (reduction) of the vanadium alkoxide turning the solution green and inducing some precipitation. These circumstances prompted MeOH and water to be used as solvents. Vanadium alkoxides were hydrolysed in water/MeOH solutions with water to vanadium alkoxide molar ratios of 3 and  $> 100$ . Both solutions had a deep red color, which eventually faded to an orange color. The films obtained from these solutions were cloudy. Additions of cyclopentanone did not cause any reduction of  $V^{+5}$  since the alkoxide was already fully hydrolysed. These solutions were cast as thin, clear, orange films which turned yellow-greenish after exposure to heat and air after a few hours and days, respectively. When hydrolysing vanadium tert-amylaldehyde oxide the alcohol of choice was t-amyl alcohol.

The hydrolysed vanadium complexes did not mix well with solutions of PAN/DMF (5% wt was commonly used). Since the PAN polymer was not readily soluble in any other solvent other than DMF, attempts were made to find conditions for vanadium alkoxide hydrolysis using DMF. All attempts resulted in cloudy or precipitated solutions. Therefore, a minimum amount of water had to be used to hydrolyse the vanadium alkoxide in order to make it soluble in the PAN/DMF solutions. The vanadium complex must also be fully hydrolysed before any DMF

can be added to this solution or precipitation will occur. On the other hand, the hydrolysed vanadium is soluble in water. It seemed possible that a precise amount of water could be used in developing a workable protocol; this was accomplished by the following procedure:

Vanadium tri(isopropoxide) oxide (VIPO, 200 mg) was mixed with 1.485 g of water until the solution remained clear. Four drops of hydrolysed VIPO was added to 1.9 g of 2% PAN in DMF and 100 mg water ( this amount of water is the highest which could be used without causing the precipitation of PAN). Another few drops of hydrolysed VIPO was added followed by more water until precipitation occurred, at which point, more VIPO was added. This procedure was repeated until the desired amount of hydrolysed VIPO was present in the solution. The solution must be stirred continuously and fast. In addition, the solution can not be filtered since it will cause the gel to be separated. The solution is allowed to stir for 2 hours during which it gains in viscosity. As long as the solution is kept free of colloidal gels, the resulting film will remain clear and will not crack. The film must be dried slowly in the oven under an inert atmosphere.

#### **d. Composite films containing PTV and DMPPV**

All films were prepared either by the spin coating or casting methods; the latter being used when thicker films were required. After coating the glass substrates with appropriate polymer and/or inorganic oxide composite, it was allowed to dry under one or more of the following conditions: air, argon, applied heat, and under pressure. Thicker films showed a tendency to cloud, crack or produce an uneven surface.

##### *d.1 Pure PTV films.*

Pure PTV films were cast from 1% (wt) solutions of the polymer precursor in DMF,  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and THF. Most films remained very non-uniform and had small particles which were most likely crystallites of reaction byproducts (salts). The majority of these particles were removed by extracting them with water from chloroform solutions and drying them over magnesium sulphate. Films prepared from salt free solutions showed good uniformity. They were subsequently subjected to heat treatment (200-250 °C), some in the presence of gaseous HCl which catalyses the reaction converting the polymer precursor to its final form. Films produced using these techniques were reddish-purple with a golden luster.

##### *d.2 PTV/PAN films.*

While the PTV films were of good quality under the best conditions, the addition of another polymer greatly improved the optical quality of the PTV films and relaxed the conditions of their preparation. Small amounts (<20% wt.) of poly acrylonitrile were added to PTV polymer precursor solutions resulting in cast or spin coated films of excellent uniformity, capable of being prepared as thick films, and which exhibited good optical quality. UV-Vis spectra revealed a band (characteristic of the PTV polymer) after the film was treated at elevated temperatures.

#### *d.3 Vanadium oxide( alkoxide)/ PTV/PAN films.*

The addition of vanadium isopropoxide oxide (VIPO) to PTV/PAN mixtures produced clear, yellow colored thick films. In this procedure 2.0 g of 1% soln. of PTV precursor in DMF was mixed with 2.5 mg of PAN in DMF, and with 20 mg of VIPO. Mixture was stirred for 10 minutes and subsequently used to make films. Cast films treated at up to 250 °C were brownish-yellow. Unfortunately, good optical quality PTV/vanadium oxide films were unattainable without the addition of PAN which resulted in high quality composite films.

#### *d.4 DMPPV/Vanadium oxide films*

A blend of dimethyl substituted PPV polymer with vanadium oxide was prepared as follows: a 1% (wt.) DMPPV precursor/chloroform solution was mixed with VIPO producing composites that were from 10% to 50% (wt.) DMPPV ("weight percent" relates the mass of the precursor to the mass of vanadium pentoxide after hydrolysis of VIPO). After mixing the DMPPV precursor with VIPO, the solution was cast on slides and allowed to dry. The dried films were clear, uniform, and exhibited a green color indicating presence of  $V^{+4}$  ions. UV-Vis spectra revealed major absorption bands at about 1.3  $\mu\text{m}$  and at .7 $\mu\text{m}$ . When the samples were treated with heat in an inert atmosphere (argon), the low energy band disappeared (the absorption was most likely due to the presence of -OH species from water or alcohols) while the high energy band was red shifted by about 200 nm. It should be noted that films processed in the presence of oxygen did not show a well defined absorption band at 800 nm, rather, only a slowly descending shoulder of the absorption band was present.

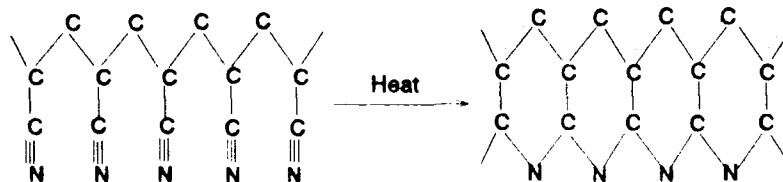
## 4. SPECTROSCOPY AND CONDUCTIVITY

Each of the prepared films was subjected to further analysis which included one or more of the following: (i) measurement of the absorption profile, usually in the range 400 nm to 1700 nm, (ii) measurement of the sample's conductivity, and (iii) measurement of third order optical susceptibility  $\chi^{(3)}$ . Conductivity measurements were generally performed on two samples of the same composite subjected to different heat treatments to assess the degree of polymer oxidation by vanadium pentoxide. Degenerate Four Wave Mixing, using 602 nm subpicosecond (400 fs) amplified pulses were performed only on samples exhibiting reasonably low absorption at the measuring frequency. Samples having high absorption have a tendency to burn upon testing even at moderate input powers. In addition, very strong resonance enhancement of the conjugate signal prevents a routine and accurate assessment of the sample's actual optical nonlinearity.

### 4.1 Measurement Techniques

#### a. UV-VIS Spectroscopy

The aim of UV-Vis studies was to explore the electronic structure of the composites made of  $V_2O_5$  and poly (thienylene vinylene), poly (acrylonitrile) and poly (dimethoxyphenylene vinylene). In these type of blends, the polymer is expected to be in the oxidized form as a result of its interaction with  $V_2O_5$ . These specific polymer-oxide interactions may result in the formation of a charge transfer band which can be conveniently detected in the electronic spectrum of the blends. In the case of poly (acrylonitrile)/vanadium pentoxide blend, the oxidation process was expected to take place after thermal conversion of the polymer to a ladder polymer (see Figure 7 below) with a band gap of much lower energy than unconverted poly (acrylonitrile).



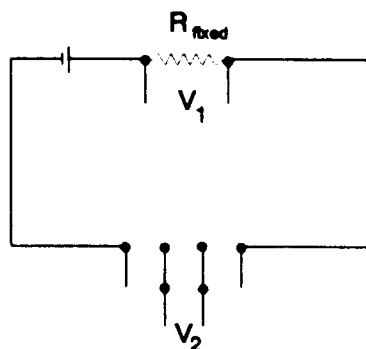
**Figure 7** Thermal conversion of poly (acrylonitrile) to ladder polymer.



## b. Conductivity Measurements

The conductivity measurements were initially performed using the four probe method. In this method, four electrodes are placed on the sample either by vacuum deposition of a thin metal film (gold, silver, chromium etc.) through a patterned mask or by applying a conductive silver epoxy. Using a precision electrometer, one measures the current or voltage between the inner and outer pairs of electrodes, as shown below. In the equations of Figure 7,  $\sigma$  is the material conductivity (Simens/cm),  $l$  spacing between the probes (electrodes) and  $A$  stands for the sample's cross sectional area.

The four probe method is a convenient method of obtaining some preliminary results but, is not the most appropriate geometry since it is most useful when performed with samples exhibiting minuscule conductivity and due to the fact that the measured conductivity is often affected by surface effects. For these reasons, subsequent measurements were performed by direct monitoring of current flowing through the composite film. All films subjected to conductivity measurements were deposited onto glass substrata (coated with a commercially obtained, transparent and conductive layer of indium-tin oxide (ITO)) using either the spin coating or casting technique. Subsequent heat treatment was carried out in a temperature controlled oven under an inert atmosphere (argon or nitrogen). In this arrangement, the ITO layer deposited onto the glass substrate served as one electrode and a vacuum deposited silver film on top of composite film served as the second electrode.



$$R_x = \frac{V_2}{I} \quad I = \frac{V_1}{R_{fixed}}$$

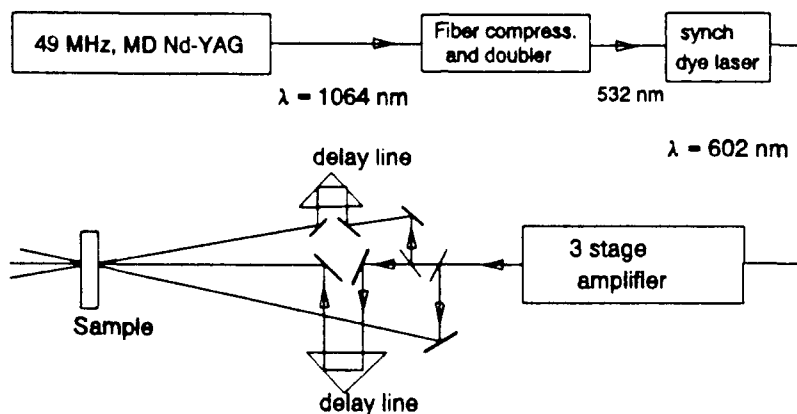
$$R_x = \frac{V_2}{V_1} R_{fixed}$$

$$R_x = \frac{1}{\sigma} \frac{l}{A}$$

**Figure 8** Schematic representation of four probe conductivity measurement.

### c. Third Order Optical Susceptibility Measurement

All experiments to assess third order nonlinear optical susceptibility were performed utilizing 400 femtosecond pulses generated by synchronously pumped (mode locked at 49 Mhz Nd-YAG laser, fiber compressed) dye laser radiation (602 nm). The pulses were amplified with use of three stage amplifier, appropriately attenuated and split in three beams to form nonplanar forward Degenerate Four Wave Mixing experimental arrangement allowing precise measurement of optical third order nonlinearity. The above equipment, located at Photonics Research Laboratory, SUNY University at Buffalo, was used on facility lease agreement.



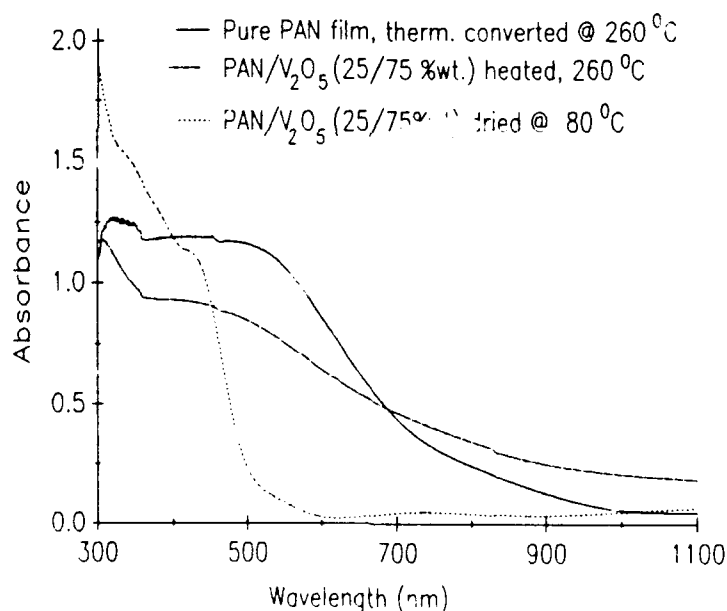
**Figure 9** DFWM experimental arrangement

The produced polymer/ $\text{V}_2\text{O}_5$  composites exhibited high optical densities at visible frequencies. This led to strong resonance enhancement of the conjugate signal, and, in instances of films thicker than approximately  $0.5 \mu\text{m}$ , to thermal degradation (burning) of the sample. Therefore studies were performed only on those samples of relatively low optical density and/or those that were very thin.

## 4.2 Results and Discussion

### Electronic spectra of PAN/V<sub>2</sub>O<sub>5</sub> composites.

Poly (acrylonitrile) polymer undergoes structural changes upon careful thermal treatment (pyrolysis) above 200 °C and converts to a ladder type of polymer. Such cyclization introduces characteristic changes in the electronic spectrum. Absorption of light in a ladder structure should lead to formation of excitons-excitation across the low energy shifted band gap (ca. 1.7 eV after pyrolysis vs. 3.5 eV before heat treatment). In a way similar to the well-known one-dimensional  $\pi$ -electron conjugated polymers, the lattice will deform and the single and double bond lengths will change to adapt to the new charge distribution. The excitation formed in this way is called an exciton which may have a character of bipolaron, i.e. a thermalized charge carrier geminate pair.



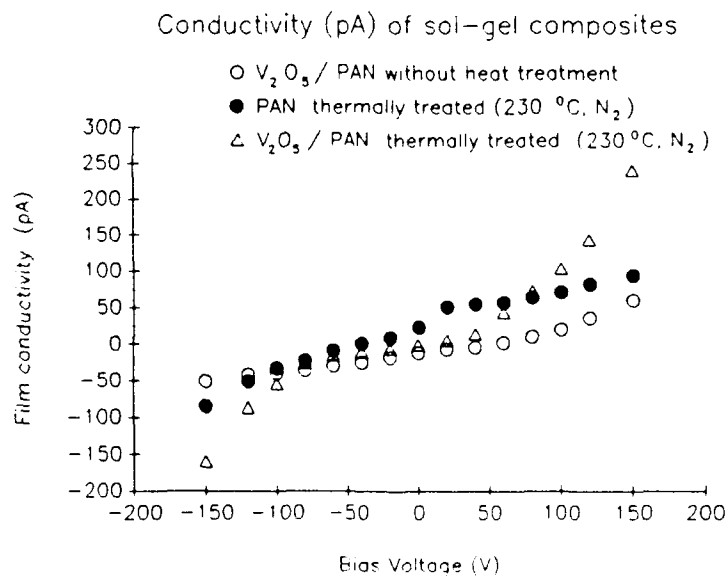
**Figure 10** Electronic spectra of thin films of converted PAN polymer and its blend with vanadium gel.

Representative electronic spectra of pyrolyzed PAN and PAN/V<sub>2</sub>O<sub>5</sub> composite are shown in Figure 10 which also shows the spectrum of the composite before heat treatment. As one can

see, the dominant changes in the absorption profile are due to changes in the polymer structure. Because of the absorption tail extending far into the near IR region it is extremely difficult to observe any possible charge-transfer band which could have arisen from polymer oxidation by vanadium pentoxide gel. However, if indeed such process occurred it should detectably change (increase) the conductivity of the blend with respect to pure polymer. This will be discussed in the next section.

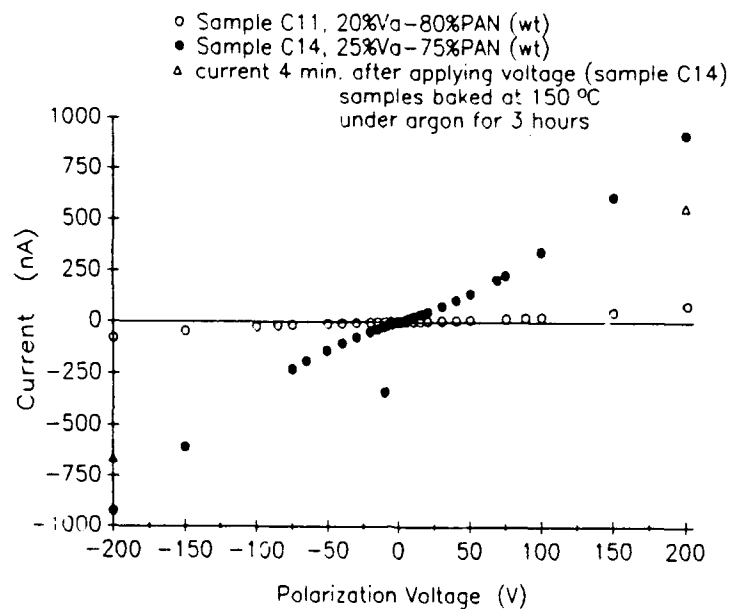
### Conductivity of PAN/ $V_2O_5$ composites.

Figures 11 through 15 display current-voltage characteristics of polyacrylonitrile/vanadium oxide composites with different relative ratios of polymer to the oxide. Part of the measurements were recorded on samples before and after the heat treatment to investigate possible oxidative charge transfer process which should result in enhanced conductivity.

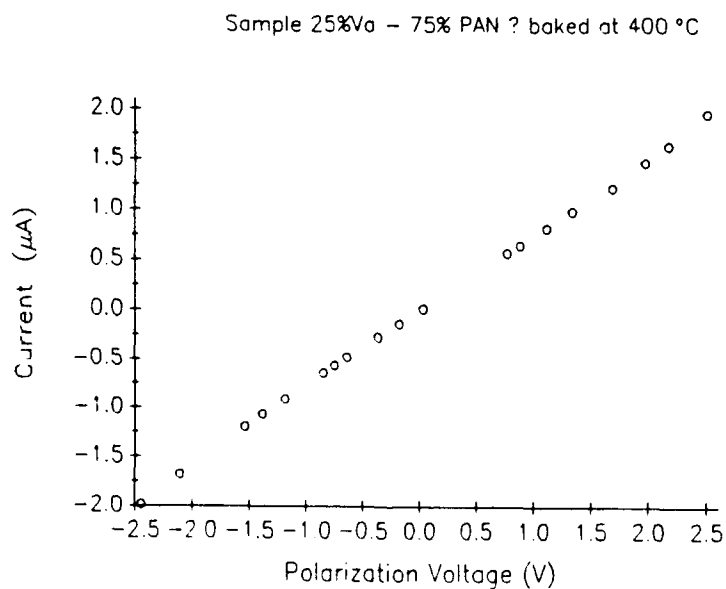


**Figure 11** I-V plot of PAN/ $V_2O_5$  composites. Measurement was performed in coplanar geometry.

It can be seen from the results that cyclization of polyacrylonitrile along with addition of vanadium oxide gel introduce characteristic changes in the electrical properties of the composite material. Typical experimental results of electrical conductivity measurements exhibit an increase in the conductivity with an increased concentration of vanadium oxide gel in the blend. This behavior



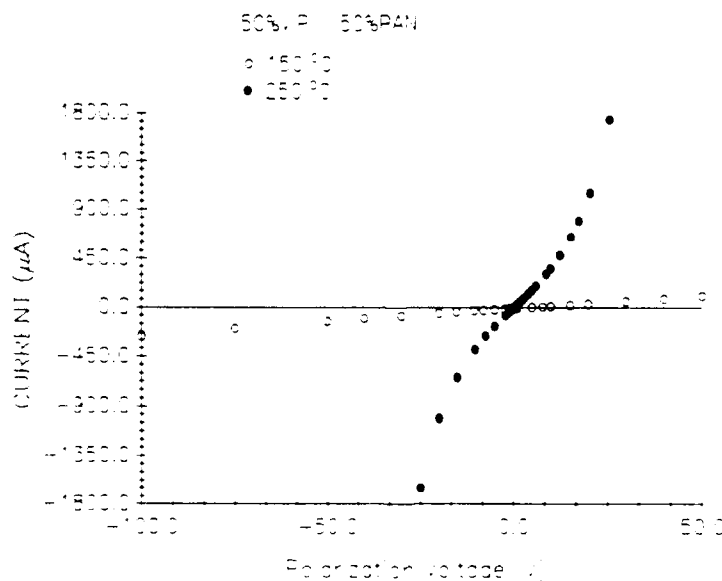
**Figure 12** I-V characteristics of PAN/V<sub>2</sub>O<sub>5</sub> blends with low content of oxide.



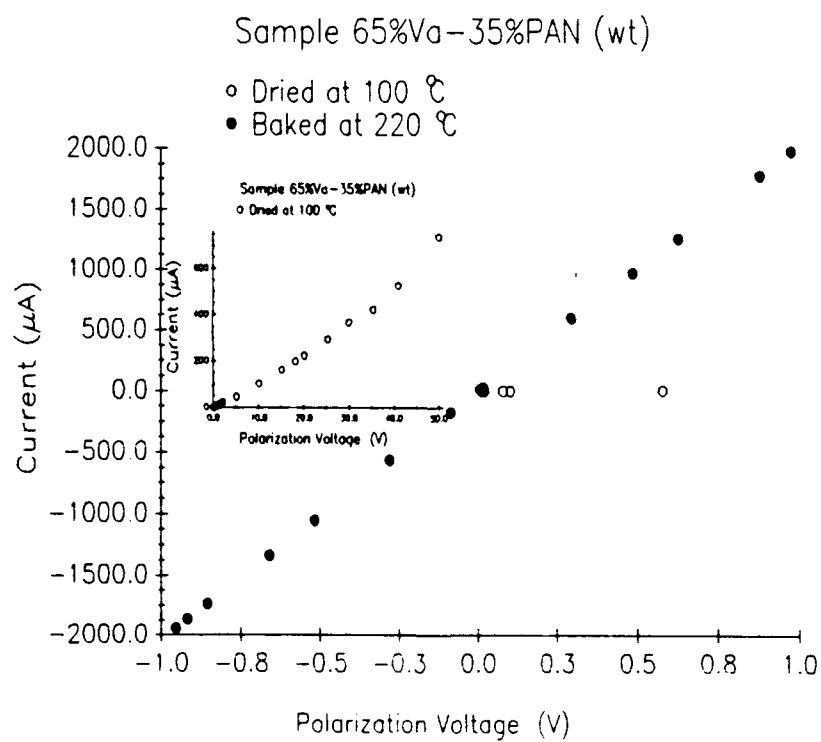
**Figure 13** I-V curve of 25% V<sub>2</sub>O<sub>5</sub>/75% PAN composite baked at 400 °C.

is similar to one featured by doped polymers, whereupon doping introduces charged species on the polymer chain. However, there is also an increase in the electrical conductivity with the degree of cyclization of polyacrylonitrile polymer, even without the dopant. This increase may be correlated to the change in the conjugation of the polymer chain. It was already observed that this structural transformation leads also to  $\chi^{(3)}$  from the  $\pi$ -electron band transitions and polaron absorption<sup>12</sup>. Table 1 summarizes the experimental conductivity data performed on polyacrylonitrile/ $V_2O_5$  composite films. It is evident that the increase in conductivity depends on two factors: (1) extent of cyclization of the polymer, and (2) concentration of vanadium oxide in the composite. This also signifies the importance of the processing parameters in the sol-gel preparation procedure of fabricating composite materials. The exact properties of the final material can be attained by designing the material's composition and precisely controlling the fabrication process.

It should be mentioned that conductivity mechanism observed in fabricated PAN/vanadium oxide composites has not been fully explored. To understand the potential and possible applications of these new materials, some additional work needs to be done to establish temperature dependence of the conductivity, the useful range of the composites' constituents to attain the material's multifunctionality: high optical quality, mechanical and environmental strength while retaining enhanced conductivity. These features are decisively important in designing composites for photorefractive materials, antistatic coatings, electroluminescent display panels, light emitting devices etc.



**Figure 14** I-V curve of 50/50 (wt) PAN/ $V_2O_5$  blend showing the effect of heat treatment.



**Figure 15** I-V curve of 35% PAN/65% V<sub>2</sub>O<sub>5</sub>. Inset: I-V curve of low temperature dried sample.

**Table 1** Conductivity of PAN/V<sub>2</sub>O<sub>5</sub> composites

COMPOSITION AND THERMAL TREATMENT	CONDUCTIVITY simens cm <sup>-1</sup> x 10 <sup>8</sup>
100% PAN, thermally converted	1
90% PAN/10% V <sub>2</sub> O <sub>5</sub> , dried @ 60 °C	1
90% PAN/10% V <sub>2</sub> O <sub>5</sub> , partially converted	4
80% PAN/20% V <sub>2</sub> O <sub>5</sub> , partially converted	0.26
75% PAN/25% V <sub>2</sub> O <sub>5</sub> , partially converted	6
75% PAN/25% V <sub>2</sub> O <sub>5</sub> , fully converted	20.5
50% PAN/50% V <sub>2</sub> O <sub>5</sub> , partially converted	7.2
50% PAN/50% V <sub>2</sub> O <sub>5</sub> , fully converted	170
35% PAN/65% V <sub>2</sub> O <sub>5</sub> , partially converted	48
35% PAN/65% V <sub>2</sub> O <sub>5</sub> , fully converted	5000

It should be mentioned that several PAN blends with vanadium oxide gels exhibited photoconductivity features which in light of an increased charge carrier mobility in these composite materials, makes them excellent candidates for applications as the photorefractive medium.

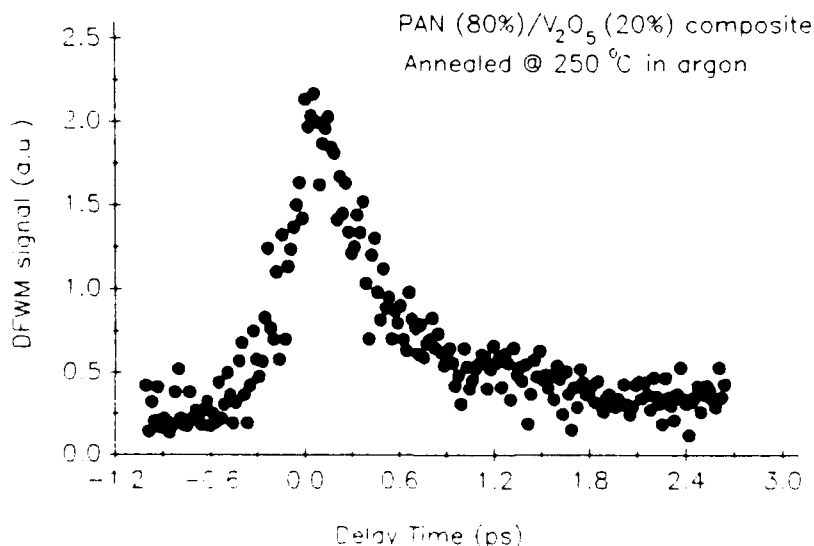
### Third order optical nonlinearity

DFWM experiments were carried on selected samples of pyrolyzed polymer/oxide blends. A representative result is depicted on Figure 16, for a composition of 80% wt. of polymer. In general, the four wave mixing signals were obtained using the forward geometry with CS<sub>2</sub> as a standard. However, since the working frequency lies in the region of absorption (linear



absorption coefficient  $\alpha$  is in the range  $3 \cdot 10^3$  to about  $7 \cdot 10^8 \text{ cm}^{-1}$ ) the observed conjugated beam signal comprises resonant one-photon electronic processes. The signals may be considered to arise from changes induced in both the real and imaginary parts of complex susceptibility  $\chi^{(1)}$ . This means that both the real and imaginary parts of the refractive index and the absorption coefficient of the sample can be altered by the instantaneous interaction of the optical fields through the third order susceptibility  $\chi^{(3)}$  and the formation of excited species. The former, being of an electronic nature, persists for the optical pulse duration; the latter is not, on the other hand, instantaneous since the lifetime of excited species are governed by radiative and nonradiative relaxation times. This gives rise to a conjugate signal persisting much longer than the pulse duration. This effect is exemplified in Figure 14 as a tail lasting a few picoseconds after zero time. The effective  $\chi^{(3)}$  values obtained for these samples, estimated by comparing the intensity of the DFWM signals of the composite films with that of a reference ( $\text{CS}_2$ ) and correcting for the absorption losses, were in the range of  $7 \times 10^{12} \text{ esu}$  to  $3 \times 10^{11} \text{ esu}$ .

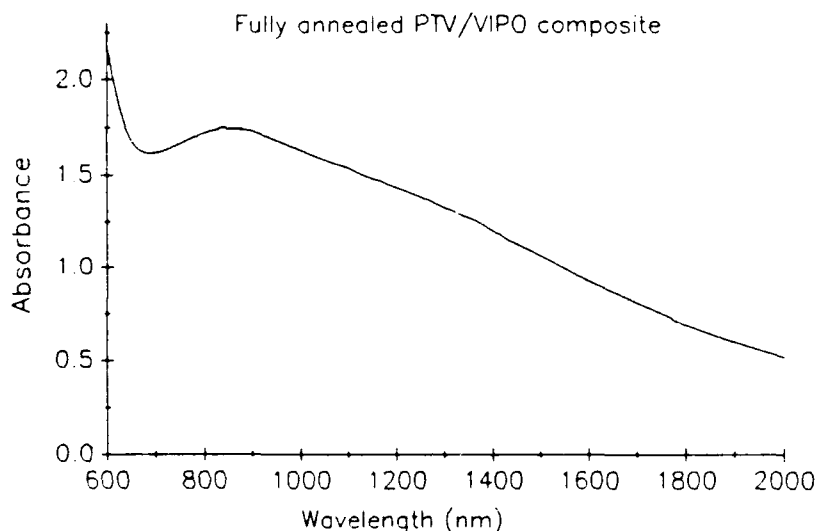
Partially converted composite films which possessed much less absorption at the sampling wavelength also produced DFWM signals although, in this case, formation of the permanent grating was observed in a very short time, less than 15 seconds.



**Figure 16** Representative DFWM signal acquired from 80% PAN-20% V<sub>2</sub>O<sub>5</sub> composite annealed at 250 °C.

### Electronic spectra of Poly(arylene vinylene)/ $V_2O_5$ composites.

The pure polymer precursor films of PTV and DMPPV were of a yellowish color and showed weak absorption in the visible frequencies at around 3.5 eV, while thermally converted polymer films featured a strong absorption band associated with the  $\pi$ - $\pi^*$  transition (see Figure 6).

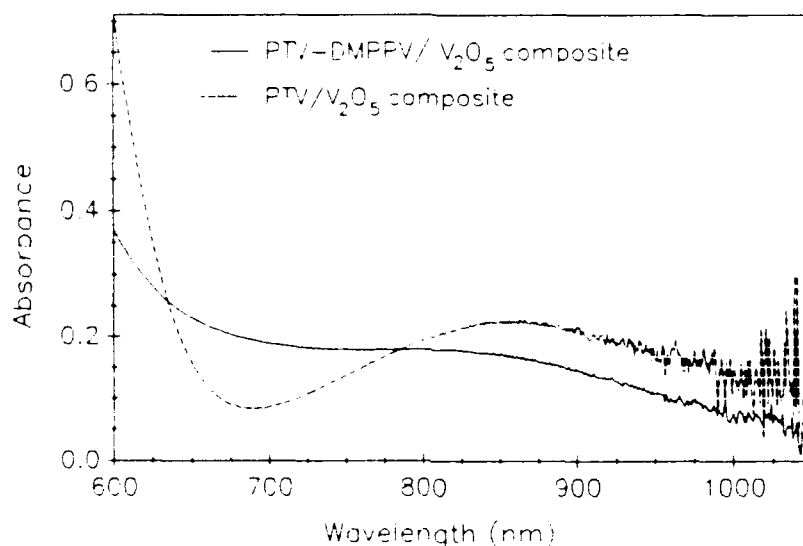


**Figure 17** Electronic spectrum of fully converted PTV/ $V_2O_5$  (65% / 35% wt.) composite.

The shape of the absorption profile reflects to certain extent, the distribution of the  $\pi$ -conjugation length. In general, the band gaps of these polymers are located in the range of 2.0 eV to 1.75 eV.

Sol-gel microcomposites fabricated from vanadium alkoxides oxides and PTV, DMPPV or mixed PTV-DMPPV polymers showed increased absorption in the visible range which extended to near IR. They also displayed absorption characteristics which indicated that a specific interaction between vanadium oxide and polymer(s) could take place. It is seen in Figure 17 which shows the electronic spectrum of about 5  $\mu$ m thick film of PTV/ $V_2O_5$  blend with an absorption band centered at about 850 nm. This band is not observed neither in spectra of pure (and converted) polymers nor in the vanadium oxide gels. Figure 18 presents visible spectra of thinner films (less than 1  $\mu$ m) prepared from PTV and mixed PTV-DMPPV (50/50 % wt.) polymers and vanadium alkoxide oxide and thermally converted at 250  $^{\circ}$ C in the presence of

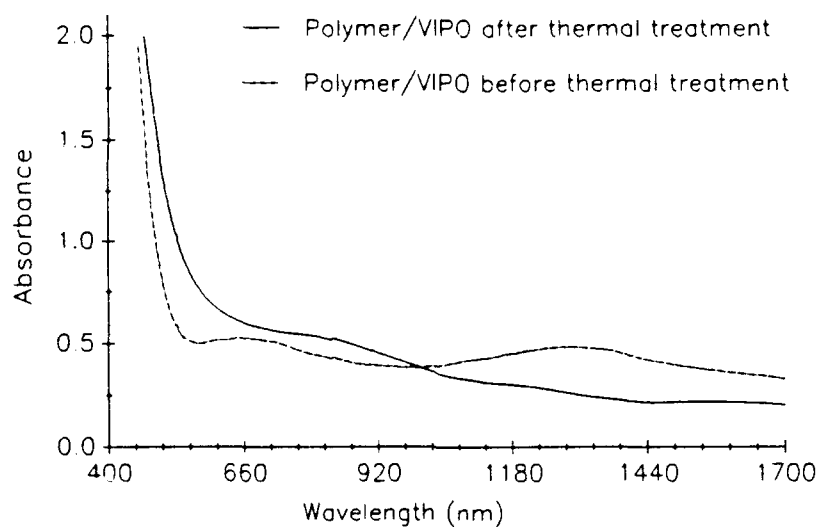
inert gas (argon). Both spectra reveal a similar pattern, ie. the main absorption with onset at about 700 nm is accompanied by an additional, relatively weak absorption band centered around 850 nm. This feature may be assigned to the charge transfer band associated with oxidation of



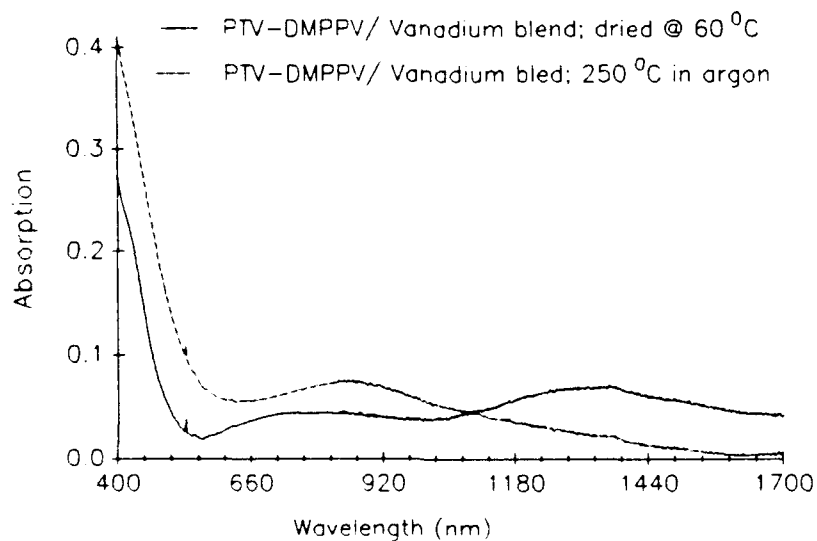
**Figure 18** Electronic spectra of vanadium oxide blends with poly(thienylene vinylene) and poly(2,4-dimethoxyphenylene vinylene)

conjugated polymer network by vanadium oxide. The formation of an oxidized polymer- $V_2O_5$  network by oxidative polymerization of some organic molecules by vanadium pentoxide gels, yielding conductive materials as has already been observed. In this process, part of the  $V^{+5}$  sites in the vanadium pentoxide gel network has been reduced to  $V^{+4}$  sites, thus establishing a possible path for charge transport. Conductivity of the resulting material depends greatly on polymer/vanadium pentoxide ratio.

Spectroscopic investigations on numerous samples of PTV and PTV-DMPPV/vanadium alkoxide blends conducted at LPT, Inc. revealed that, indeed, reduction of  $V^{+5}$  species to  $V^{+4}$  species took place and was evidenced by the appearance of a new absorption band. As shown in Figure 19, freshly prepared composites of PTV and PTV-DMPPV with vanadium alkoxide oxides displayed two distinct absorption bands located at about 2.1 eV and 0.89 eV, the latter being associated with the strong absorption in the near IR frequencies by hydrolysis by-products: water and alcohol. Upon further thermal treatment necessary for the full conversion of PTV and DMPPV precursors and the removal of reaction by-products, this band disappeared. The high energy band, on the other hand, shifted to lower energy, being centered at ca. 850 nm (1.5 eV).



**Figure 19** UV-VIS spectra of PTV/ $V_2O_5$  blend before and after thermal conversion of the polymer precursor.



**Figure 20** UV-VIS spectra of PTV-DMPPV/ $V_2O_5$  composites without and with thermal treatment.

### Conductivity of poly(arylene vinylene)/ $V_2O_5$ composites.

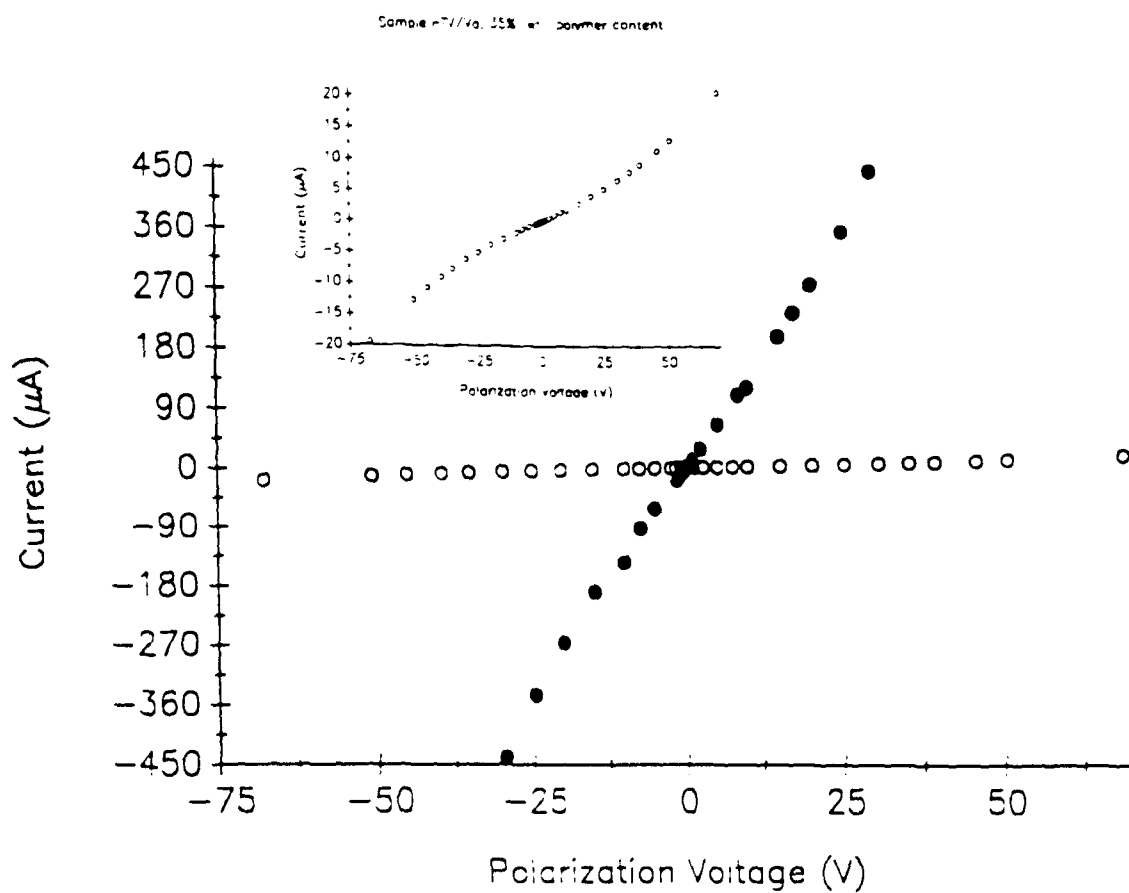
The intrinsic conductivities of pure PTV and DMPPV polymer films at room temperature are between  $10^{-14}$  to  $10^{-16}$  siemens  $cm^{-1}$ . These values can be increased by a few orders of magnitude using appropriate dopants and/or by stretching the films. For example, iodine doped PTV films showed conductivities as high as 1 siemens  $cm^{-1}$ . However, conductivities of the doped polymer films tend to be unstable since the dopants are usually of high reactivity towards atmospheric moisture (as  $AsF_5$ ) or volatility (as iodine). On the other hand, conductivity of the polymers produced from their precursors via elimination reaction depend on the extent of conversion of precursors to conjugated structures. The largest conductivities have been frequently achieved in partly converted films of PTV and DMPPV. Thus, the quest to achieve maximum conductivity in these type of polymers appears to be a more complex task involving not only the mechanism of charge transport, but also the effect of the band structure and composition.

Representative experimental results of the conductivity measurements performed on several  $\chi^{(3)}$  polymer/ vanadium oxide blends of different compositions are presented in Figures 21 to 23. In all instances, investigated samples were fully or partly thermally converted with the exception of one sample (Figure 22, inset) which was only dried at about 60 °C. In the latter case, as well as for a number of other similarly prepared samples, the observed unusually high conductivity may be attributed to ionic conductivity; all of these types of samples also showed very unstable currents and very low dielectric breakdown, which might result from electrochemical reactions on the electrodes.

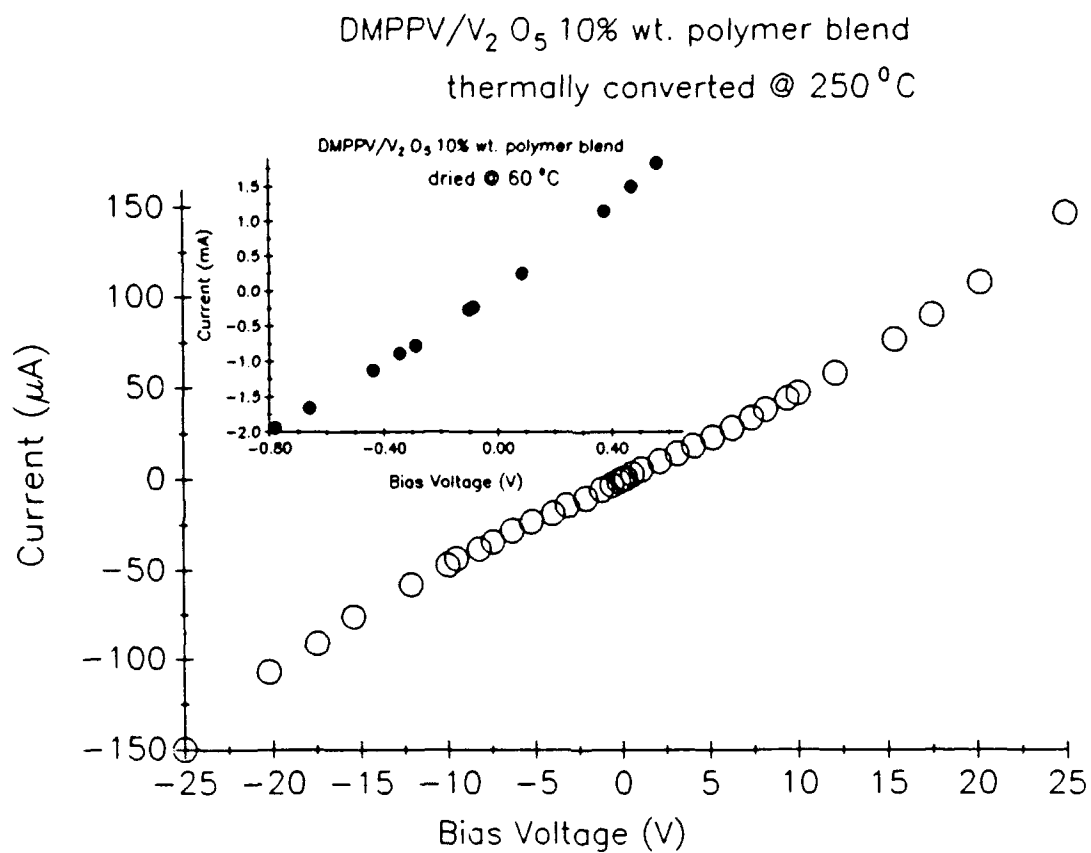
The remaining current voltage characteristics display, in general, an enormous increase in the composite film conductivities with respect to pure polymers or even pure vanadium pentoxide gels, whose conductivity ranges from  $10^{-6}$  to  $10^{-4}$ , depending upon the preparation method. However, the dependence of the blend composition (i.e. relative concentration of polymer to vanadium oxide) on the conductivity does not exhibit a clear trend. For example, similar samples prepared with help of different solvent mixtures, like methanol/DMF and CP/DMF, frequently showed drastically different conductivities. This, in our opinion, may be due to the very reactive nature of vanadium alkoxides used in the preparation process; vanadium alkoxides could react with less stable solvents (CP) to create entirely new species responsible for the observed increase in apparent conductivity. Table 2 summarizes the results of these measurements.

The results presented here demonstrate that the conductivity of the organic semiconductors (i.e. conjugated polymers) can be enhanced by many orders of magnitude by combining them with inorganic semiconductor ( $V_2O_5$ ) using sol-gel processing technique.

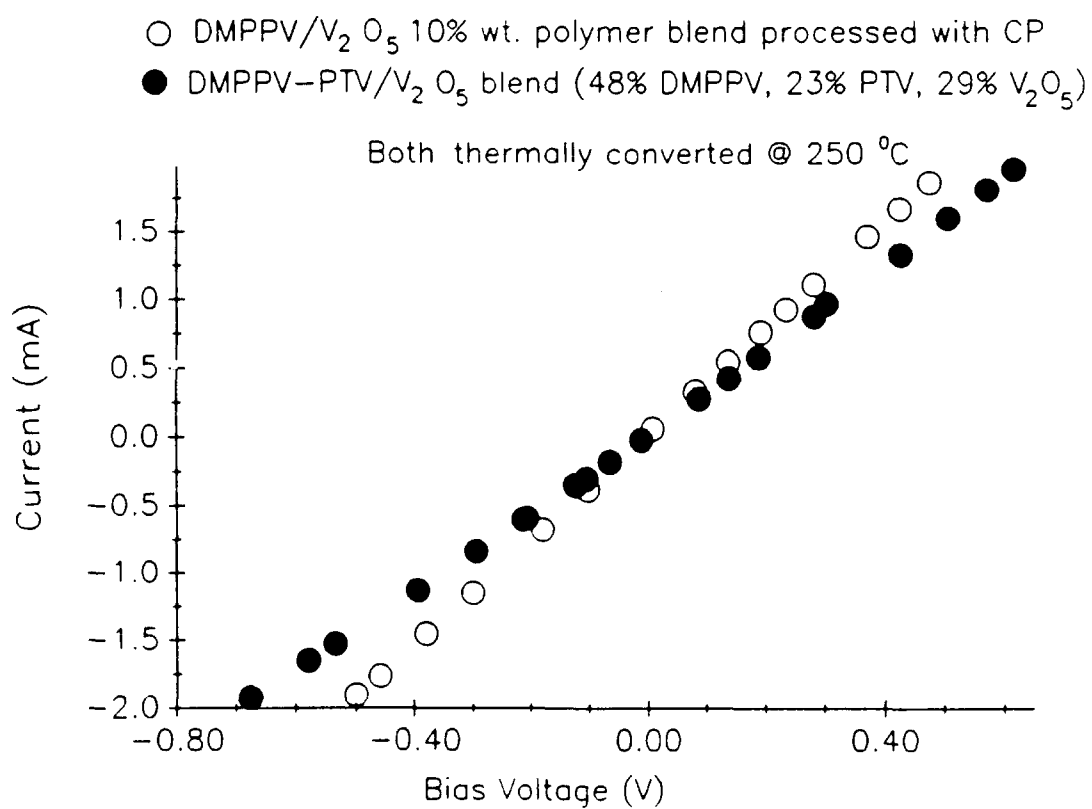
- Sample PTV/Va, 35% (wt.) polymer content
- Sample DMPPV-PTV/VA, 50% (wt.) polymer content



**Figure 21** Current-Voltage curve for two different sol-gel composites consisting of  $\chi^{(3)}$  polymer and vanadium oxide gel.



**Figure 22** I-V curve of DMPPV/ $V_2O_5$  composite annealed at 250 °C. Inset shows data for the sample dried at 60 °C.



**Figure 23** I-V characteristics of PTV and mixed PTV-DMPPV polymer/oxide ( $V_2O_5$ ) composites.

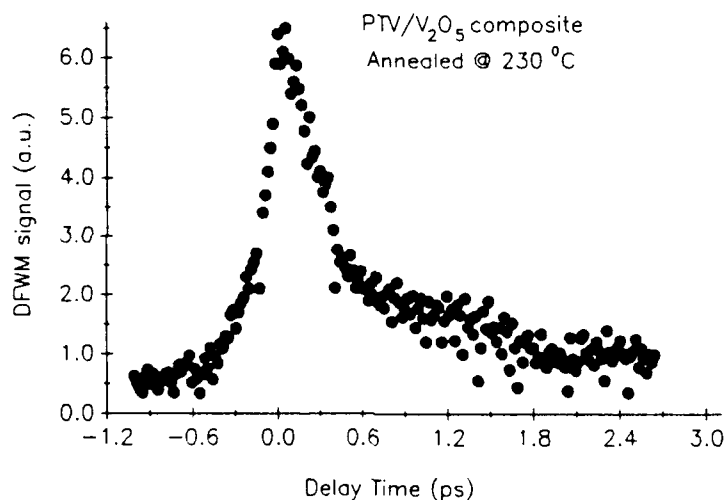


**Table 2.** Conductivities of PTV and mixed PTV-DMPPV polymer composites with  $V_2O_5$ .

POLYMER/OXIDE BLEND COMPOSITION	CONDUCTIVITY Simens $cm^{-1} \times 10^5$
90%DMPPV-10% $V_2O_5$ not converted	1400
90%DMPPV-10% $V_2O_5$ converted	3.4
90%DMPPV-10% $V_2O_5$ converted, CP used	2300
70%(DMPPV-PTV)-30% $V_2O_5$ converted	1600
50%(PTV/DMPPV)-50% $V_2O_5$ converted	9.4
35%PTV-65% $V_2O_5$ converted	0.2

## DFWM experimental results.

Conjugated polymers as ladder polymers, polydiacetylenes and, in particular poly(arylene vinylenes) have been recognized amongst the organic materials as being the best candidates for numerous applications in photonics technology. This recognition arises from the fact that these polymeric materials show very large values of nonresonant third order nonlinear susceptibility,  $\chi^{(3)}$  leading to very fast response times. However, polymers, being by nature of low mechanical strength and susceptible to environmental (chemical in particular) degradation, in many instances are not suitable as active media in commercial devices. One of the intentions of this Phase I effort was to assess whether these type of polymers, combined by sol-gel processing technique with  $V_2O_5$  network - a strongly oxidizing inorganic matrix - preserve their nonlinear optical properties.



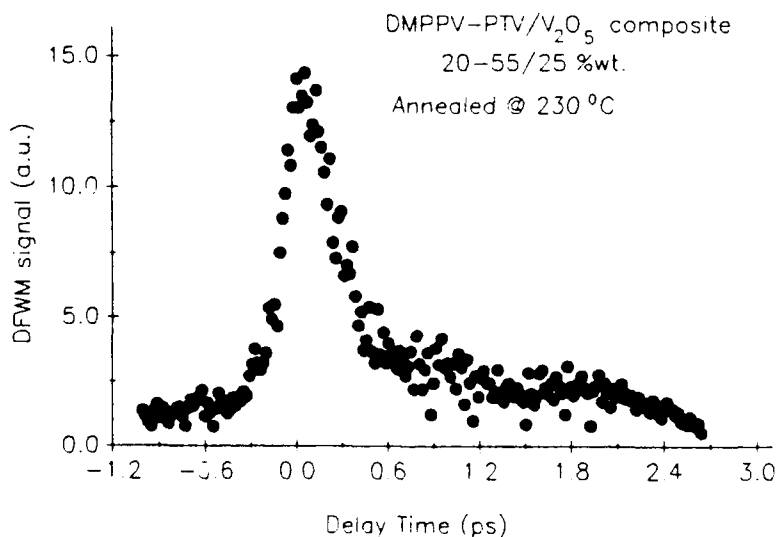
**Figure 24** DFWM signal of PTV/ $V_2O_5$  composite vs. delay time of the probe beam.

Figures 24 and 25 show typical DFWM signals obtained from PTV/ $V_2O_5$  and PTV-DMPPV/ $V_2O_5$  composite films. In general, DFWM signals from thin films of fully converted polymer/oxides composites were relatively strong. The stronger signals were obtained from composite samples containing DMPPV polymer rather than the PTV polymer. In the case of mixed polymer composites consisting of PTV and DMPPV polymers, signals were proportionally increasing with the increase of DMPPV content. It was, in our opinion, due to the fact that PTV/ $V_2O_5$  composites featured higher optical densities throughout the visible region which caused strong attenuation of the optical fields. However, the working frequency, 602 nm lies within the absorption profile of either composite, therefore observed conjugate signals involved one-photon resonance effects.

Some experiments were also performed on low temperature dried samples containing only partially converted polymers in the oxide matrix. These samples did not produce DFWM signals, as expected since third order optical susceptibility in such systems arises mainly from  $\pi$ -electron conjugation; the polymers attain their  $\pi$ -electron conjugated structure only upon high temperature treatment.

To establish the exact values of  $\chi^{(3)}$  susceptibility several parameters, like the sample's thickness and refractive index, must be known. Since our measurements were performed within the sample's absorption profile, the value of refraction index becomes complex and difficult to assess directly. Therefore, in order to give a rational estimate of  $\chi^{(3)}$  values the indices of fully converted pure polymer samples were assumed and the strength of the DFWM signals related to the signal delivered by a standard material,  $\text{CS}_2$ , of known  $\chi^{(3)}$  value equal to  $6.8 \times 10^{-13}$  esu. The effective values of  $\chi^{(3)}$  estimated in this manner were in the range of  $5 \times 10^{-11}$  to  $3 \times 10^{-10}$  (all in esu units). These values, as one might have expected, are slightly lower than those of pure polymer samples (for example PTV:  $4 \times 10^{-9}$  esu; DMPPV:  $1 \times 10^{-9}$  esu), but do indicate a strong nonlinear optical response of the novel materials.

The performed DFWM experiments established that conjugated polymer/vanadium oxide composites do form good optical quality films capable of exhibiting relatively strong  $\chi^{(3)}$  signals, and can potentially be used in photonics applications. It is important to state that further optimization of the presented processing technique is needed to achieve materials fully compatible with the applications' needs.



**Figure 25** DFWM signal vs delay time of the probe beam for PTV-DMPPV/V<sub>2</sub>O<sub>5</sub> sol-gel composite.

## 5. CONCLUSIONS AND RECOMMENDATIONS

During the six months of this research contract, the staff of LPT has accomplished a number of research objectives including the synthesis of several alkoxides and one polymer having demonstrated nonlinear optical properties, engineering a large number of composite films having good homogeneity and optical properties, and demonstrating that several of these films have high conductivity while retaining their nonlinear optical response as evidenced by DFWM results.

It has been demonstrated that sol-gel technology can be used in conjunction with organic chemicals, conjugated polymers in particular, to provide extremely useful composite materials for photonics and electronics applications. The incorporation of organic chemicals (including polymers) with inorganic glasses represents an opportunity to wed the superior conventional optical properties of silica glass and its inorganic dopants with the synthetic flexibility and nonlinear optical properties of polymers and other organic molecules. This has been evidenced by this most recent work wherein the staff of LPT has successfully fabricated vanadium oxide/conjugated polymer composites exhibiting high conductivity values.

The work performed by LPT, Inc. staff during this Phase I research effort has demonstrated the multifunctional character of composite materials consisting of inorganic and organic components, in which both components play active roles. Composites showing significant charge carrier mobility (conductivity) and nonlinear optical response have been successfully prepared. This is a very promising accomplishment which establishes a unique method of preparing novel materials for three important applications:

1. photorefractive material devices (combination of photoconductivity and nonlinear electro-optic response)
2. electroluminescent displays or light emitting diodes (electrically induced carriers, their migration and recombination to produce photons)
3. antistatic coatings (high charge carrier mobility)

Based upon the Phase I feasibility assessment, we consider the photorefractive applications very promising for the following reasons:

1. possibility of optimizing inorganic semiconductor performance for enhanced carrier mobility
2. use of organic structures with large and stable electro-optic response
3. possibility to fabricate high optical quality composite material in form of stable films or bulk configurations.

LPT, Inc. plans to submit a Phase II proposal involving continued optimization of these types of composites followed by their development for use in the applications listed above.

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